Facility Report on ISIS, with a brief Introduction to Neutron Scattering

S.M. King

Large Scale Structures Group, ISIS Facility,Rutherford Appleton Laboratory, Chilton, OX11 0QX, UK

Received 3rd December 2003; accepted in revised form 16th March 2004

ABSTRACT

The purpose of this report is to highlight to the CCP13 community the instrumentation and opportunities for neutron fibre and non-crystalline diffraction (including solution scattering) that currently exist at the ISIS Spallation Neutron Source, and some of the developments that are planned or already underway.

Introduction

Neutron scattering will be more familiar to some in the NCD community than it is to others. Consequently this report has been broken down into a number of subsections so that the reader can jump in wherever they feel comfortable.

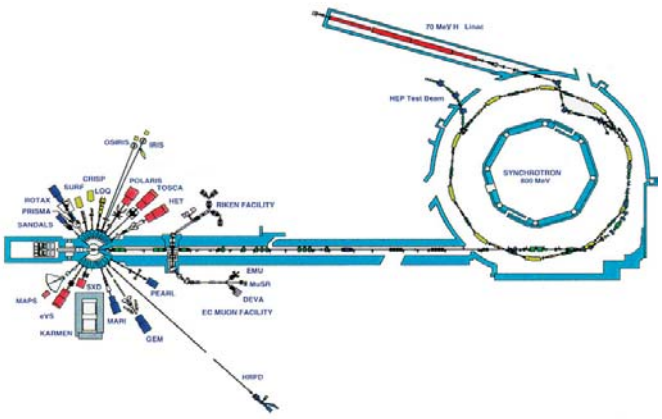

Figure 1. Schematic layout of the ISIS accelerator and neutron Target Station I. For scale, the synchrotron is 50 m in diameter. The KARMEN neutrino detector was removed in 2002/3. © ISIS.

What is ISIS?

ISIS is the name of the neutron beam research facility owned and operated by the UK Council for the Central Laboratory of the Research Councils (CCLRC) [1]. This is the same organisation that is responsible for the Daresbury Synchrotron Radiation Source and the major shareholder in the new Diamond Light Source project.

CCLRC exists to provide, maintain, and develop *large facilities* for the benefit of the UK research community, though it is always pleased to welcome international guests and partners. Use of its facilities is *free at the point of access* unless you plan to conduct commercial research. All of the major UK Research Councils have signed access agreements on behalf of the researchers that they sponsor, and a number of oversees Governments have made similar arrangements for their researchers. For further information simply contact the appropriate facility User Office. Details will be found on the relevant facility web pages.

How does ISIS work?

ISIS produces neutrons by bombarding a tungsten target with relativistic protons (travelling at 84% of the speed of light!) from a particle accelerator based around a linac and what is currently the most powerful *proton* synchrotron in the world [2]. The facility started operations just before Christmas in 1984. In order to lose energy, the excited tungsten nuclei "evaporate" sub-atomic particles, including neutrons. This process, called "spallation", is clearly very different to the only (useful) alternative method of producing neutron beams at present, nuclear fission. In turn, the way that instrumentation at the two types of source utilises the neutrons produced is subtly different. This will be expanded on later.

Though there is a preponderance of reactor-based neutron facilities over accelerator-based sources of approximately 8:1 at this time, growing environmental concerns, engineering limitations, and the age profile of the reactors will see this imbalance steadily reduce. In contrast, the future for accelerator sources is bright. The USA and Japan are presently constructing new facilities, both more powerful than ISIS, and ISIS itself is upgrading.

Time-of-flight

Anyone with experience of laboratory or synchrotron X-ray scattering will be used to the idea of working at a fixed wavelength (with a small bandpass). This is also exactly how a reactor-based neutron diffraction instrument works. A crystal monochromator or, more commonly in Small-Angle Neutron Scattering (SANS), a device called a "velocity selector", preselects a narrow wavelength band from the incident neutron distribution. As the name suggests, a velocity selector only allows neutrons with the required velocity to pass along it and onto the instrument. It works because although photons travel at the speed of light, neutrons have mass and therefore travel much more slowly! A velocity selector is, however, rather wasteful, because most of the neutrons being produced by the target/moderator assembly are being rejected by it. The

bandpass could be broadened to increase the flux at the sample, but only at the expense of degrading the wavelength and Q resolution of the instrument.

The ISIS particle accelerator produces and accelerates its protons in bunches. Consequently the neutrons are produced in pulses (at 50 Hz) and the beams have an intrinsic time structure that can be utilised. The Swiss SINQ spallation source, on the other hand, produces its protons continuously [3]. This is technologically less challenging, and allows the SINQ target to produce more neutrons per second, but because it is simply using an accelerator to emulate a reactor its instruments also need to use monochromators and velocity selectors.

On a pulsed source, as at ISIS, all it is necessary to do is to time the arrival of the neutrons to any given point; the faster (higher energy, shorter wavelength) neutrons will arrive before the slower (lower energy, longer wavelength) ones! This "time-of-flight" (tof) approach actually conveys a number of advantages over fixed-wavelength operation. Two are worth highlighting here:

Fixed-geometry instrumentation

The Q-range of any fixed-wavelength instrument is determined by the incident wavelength, the sample-detector distance, and the radial distance subtended by the detector(s). The last two factors, of course, define the scattering angle.

Now consider a detector in "transmission geometry", as is often the case in SAXS or SANS. Photons or neutrons arriving close to the centre of the detector (the "straight-through" beam) will have been scattered to small Q values and vice versa. However, because the minimum and maximum radii of the detector are fixed, the corresponding Q-range is quite small. The only ways of changing the Q-range are: (i) by changing the wavelength (but with neutrons this may adversely change the incident flux), or (ii) by changing the scattering angle; either (a) by changing the sample-detector distance (if lengthened, photons or neutrons scattered through the same angle will appear on the detector at larger radial distances and vice versa), or (b), if possible, by moving the detector "off-axis" (which is like changing the minimum and maximum radial limits).

The subtlety of a time-of-flight instrument lies in the realisation that even though the scattering angle is still determined by the sample-detector distance and the radial limits of the detector, *different wavelength neutrons* (arriving at the detector at different times) scattered through the *same angle* will have *different Q-values*! Therefore each different incident wavelength contributes part of the overall scattering pattern, and the broader the incident wavelength range, the wider the Q-range of the instrument. Since this can all be achieved without moving the detector (if needs be), time-of-flight instruments are also known as "fixed-geometry" instruments.

It is the wide dynamic Q-range of the fixed-geometry instrument that is its defining characteristic. It obviates the need to repeat measurements, backgrounds, normalisations and calibrations at different sample-detector distances that must then be overlapped (usually with different Q-resolution), and is ideal for the study of samples where there are a range of length scales or, possibly, where the length scales are uncertain.

Better Q-resolution

The Q-resolution of an instrument, $\Delta Q/Q$, the precision with which a particular "Q-point" can be determined, is largely (but not entirely) determined by the wavelength resolution, $\Delta\lambda/\lambda$. This latter quantity differs markedly between fixed-wavelength and fixed-geometry neutron instruments.

On a fixed-geometry instrument $\Delta\lambda/\lambda$ is determined by the precision with which the neutron times-of-flight can be measured. Since these are typically a few milliseconds, timing is quite straightforward with modern electronics and a $\Delta\lambda/\lambda \sim$ 5% would not be uncommon. Conversely velocity selectors typically have a *Gaussian* bandpass of ~ 8 - 20% FWHM. This already appears to make the fixed-geometry instrument look better, but to really compare like with like it is necessary to compare the standard deviation of a rectangular timing bin with the standard deviation of a Gaussian. It is then found that for a velocity selector [4]:

effective rectangular $\quad \Delta\lambda / \lambda = FWHM \times \sqrt{12} \Big/ \sqrt{8\ln(2)}$

and so the wavelength resolution of the fixed-wavelength instrument is more like 11 - 30%, quite substantially worse!

Why use neutrons?

Anyone who has never used neutrons might be forgiven for wondering what all the fuss is about. What neutrons are not is a panacea! They are not better than X-rays, nor are they any worse than X-rays. As with all experimental techniques some samples work better than others. But what neutrons do offer is an *alternative* view of a sample.

This comes about because whereas light and X-ray photons are scattered by the electrons surrounding atomic nuclei, neutrons are scattered by the atomic nuclei themselves. The consequence of this is summarised in Figure 2. That X-rays are scattered more strongly by heavier elements is, of course, widely known and no doubt familiar to the reader. Indeed, it forms the basis of the technique of isomorphous replacement in X-ray Crystallography. The problem comes when one wants to use X-rays to study samples composed of lighter elements (e.g. H, C, N, O). An even bigger problem presents itself if the

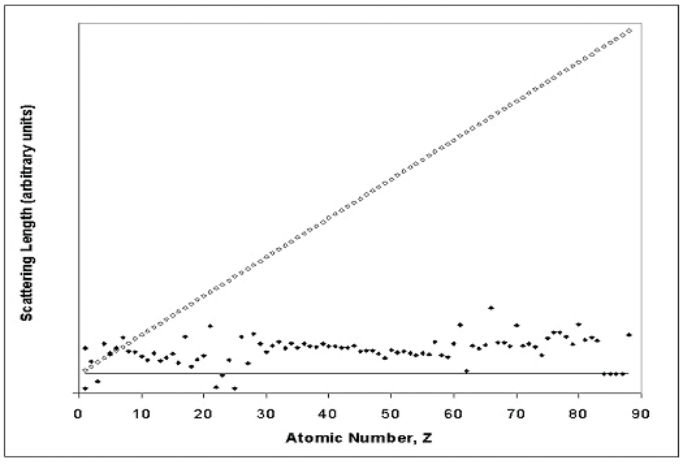

Figure 2. The relative variation of the atomic (open symbols) and nuclear (filled symbols) scattering lengths with atomic number. The continuous horizontal line marks zero scattering length.

experimental objective is to study multi-component samples (e.g. protein or polymer in solution) where all the components contain light elements. Then one component scatters much the same as any other and separating out their individual contributions is not straightforward because the "contrast" is poor.

From a first glance at Figure 2 it may not be obvious what neutrons have to offer. The answer is that with neutrons one can look at samples containing both light and heavy elements without the latter dominating the scattering. Better, the astute will have observed that elements ^{1}H and ^{2}D have nuclear scattering lengths of different sign! Why this is so (see, for example, [5]) is, though, much less important than the consequence; it means that by substituting D for H in a sample it is possible to selectively manipulate the contrast to highlight what is of interest. And, since a significant fraction of structural biology revolves around how water interacts with proteins, enzymes and nucleic acids, the potential benefits of neutron scattering to this area are enormous. On the other hand, readers who work with synthetic polymers might like to consider what could be accomplished by replacing their current organic solvent by its deuterated analogue, or by mixing normal (all-H) and deuterated versions of the monomers, and so on.

The downside is that neutrons interact much less strongly with matter than X-rays do, but even this presents an opportunity. It is possible to make neutron scattering measurements on thicker samples, or samples in metallic containers or inside quite complicated pieces of sample environment (cryostats, pressure cells, rheometers, and so on).

It goes without saying that neutrons can be produced with wavelengths that would enable the reader to probe the sorts of length scales that would be of interest to them, or that they currently probe with X-rays (a few nm to a few hundred nm). Typical "cold" neutron wavelengths range from ~ 0.1 - 2.5 nm; compare this with $Cu_{k\alpha}$ X-radiation at 0.154 nm, for example.

What will probably be less readily appreciated is the difference in the energy of the radiation. A 0.5 nm X-ray photon has an energy of ~ 2.5 keV. The energy of a 0.5 nm neutron is by comparison just 3.2 meV, 780,000 times less! Samples that might only last a few seconds in a synchrotron beam would not suffer any radiation-induced damage in a neutron beam. As an aside, instruments that measure the neutron vibrational (i.e., like IR) spectrum of a sample also exist.

Finally, in SANS, absolute intensity measurements are routine. This means that the measured cross-section data (the numbers on the "Y-axis" of a "scattering curve") can be used to derive molecular weights, aggregation numbers, thermodynamic parameters, or to improve the confidence of any model-fit. In fact SANS data has been used to put SAXS data on an absolute scale!

So what is the catch?

Well, there are two in fact. One is the cost and effort involved in using deuterium-labelled samples, though this is rarely enough to prohibit an experiment (and even then there may be alternative strategies).

The biggest single drawback with neutron scattering today is its relative lack of flux. Data collection times are typically minutes to hours, and not milliseconds to minutes as they are in X-ray scattering. But a great deal depends on the volume of, and contrast within, any given sample as some of the examples below will demonstrate.

Since neutrons cannot be focussed (at least not in the conventional sense) achieving a smaller beam footprint to study a small sample means collimating down and throwing away yet more flux. But do not get the wrong impression; beam diameters of a few millimetres are quite normal. And a small beam footprint can often be traded off against a thicker sample to improve statistics.

Small- & wide-angle scattering

ISIS has one SANS instrument, called LOQ (Figure 3). It is a traditional three-pinhole instrument and normally operates at 25 Hz, half of the ISIS frequency. This is to avoid a condition called "frame overlap" that affects all long tof beam lines, whereby short wavelength neutrons from pulse (n+1) can overtake the long wavelength neutrons from pulse (n)! The Soller bender (at short wavelengths) and the frame overlap

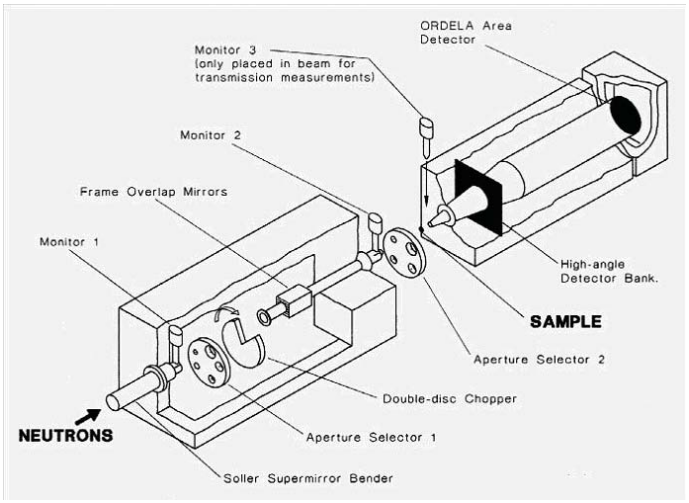

Figure 3. Schematic view of the LOQ small-angle scattering instrument. The sample position is 11 m from the cold moderator, the SANS detector is 4.1 m from the sample. © ISIS.

mirrors (at long wavelengths) in the primary collimation also help alleviate this condition. LOQ *can* operate at 50 Hz (and sometimes this is desirable, see Table 1), but only by taking a restricted wavelength range, control of which is achieved with the double-disc chopper.

As with X-rays, much of the primary and secondary collimation is evacuated (to stop the neutrons colliding with the much more massive air molecules).

LOQ has two, two-dimensional (or "area"), detectors. The SANS detector is a true multiwire ^{3}He gas detector (128 x 128 wires on a square array with 5 mm spatial resolution) manufactured by ORDELA (USA) and approximately covering $1° \leq 2\theta \leq 11°$. The High-Angle detector 0.5 m from the sample was manufactured in-house. It is constructed from 4 abutted rectangular modules (neatly avoiding the meridian & equator!),

Chopper Frequency (Hz)	Wavelength Range (nm)	Q Range (nm^{-1})	Relative Count Rate	Remarks
25	0.22 - 1.00	0.06 – 15.0	1.0	Normal operation; uses all detectors
50	0.26 – 0.67	0.12 – 2.3	1.4	Higher flux, but reduced Q-range
50	0.63 - 1.00	0.06 - 0.7	0.2	Reduces Bragg edges from short-λ

Table 1. The most common configurations of LOQ. The numbers shown assume a chopper opening angle of 126°.

each of 12 x 29 ZnS scintillator pixels, 12 mm square. This detector has an angular coverage of approximately $22° \leq 2\theta \leq 70°$, but with the virtue of tof both detectors overlap in reciprocal-space between about $1.5\ nm^{-1} \leq Q \leq 3.0\ nm^{-1}$.

The instrument is furnished with a good selection of sample environment apparatus - a thermostatted sample changer, shear flow cells, a pressure cell and a 2T electromagnet - but can additionally draw on "ISIS standard" equipment like furnaces and cryostats if needed. For solution scattering experiments samples are contained in quartz/silica cuvettes of the type normally employed in UV spectrophotometery. A recent innovation is a simple fibre specimen holder (Figure 4). Many User Groups have also developed their own apparatus. For further information the reader is directed to the LOQ web pages [6].

On April 8 2003 the UK Government announced that ISIS would get a second Target Station (TS-II), the largest investment by the Government in a single science project

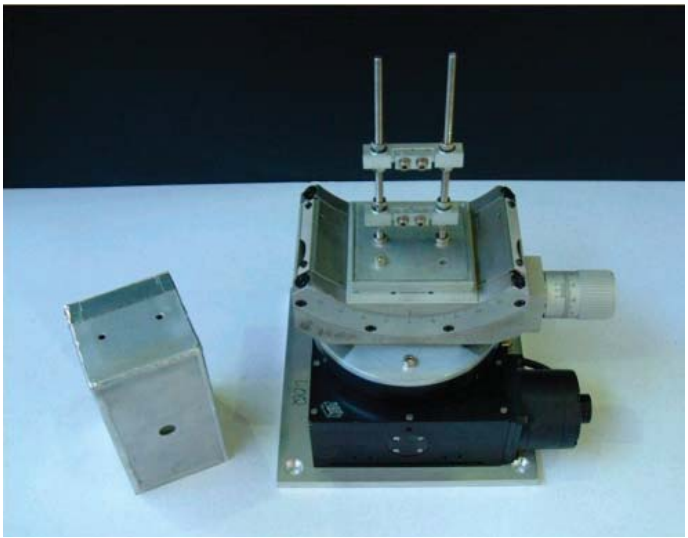

Figure 4. View of the LOQ fibre specimen holder. The ends of the sample are clamped between the two crosspieces. On the left is the cover that maintains humidity around the sample. The beam entry hole is visible on the front surface. A laser beam directed along the neutron flight path allows samples to be positioned accurately on the beamline. © ISIS.

(Figure 5) [7]. TS-II will operate at 10 Hz and is being specifically optimised towards the production of long wavelength neutrons. A new SANS instrument, currently designated SANS2b, features in the "day one" suite of instrumentation, and simulations indicate that the neutron flux at the sample should exceed that on LOQ by well over an order of magnitude.

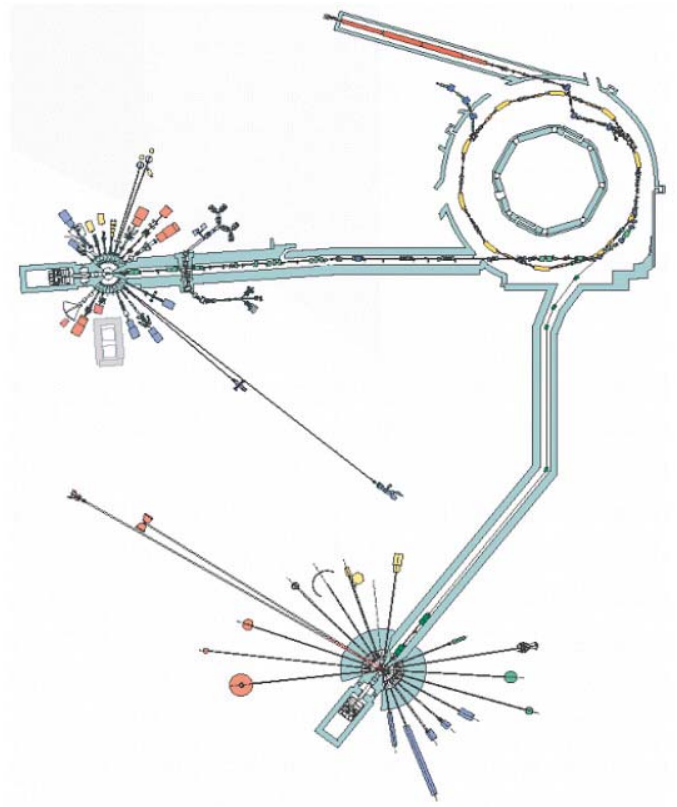

Figure 5. Schematic layout of the new Second Target Station in relation to the existing ISIS Facility. SANS2b is the long beam line in the lower-right quadrant. © ISIS.

SANS2b will be a much longer instrument than LOQ. This will allow a broader wavelength band to be utilised giving it, in turn, both a lower minimum-Q and a higher maximum-Q than is presently possible on LOQ. But the really unusual design feature of SANS2b is that it will use two, *moveable*, area detectors (each larger than the present LOQ ORDELA detector) side-by-side, with the ability to be offset vertically across their radius, in a huge "detector cave". This revolutionary design for a pulsed-source SANS instrument will offer unrivalled flexibility and dynamic range, and offer count rate improvements in the case of weakly scattering samples or experiments with more highly collimated beams, simply because there will be twice the detector area available to record the scattering pattern. SANS2b is expected to undergo commissioning towards the end of 2007. The provision of a *second* SANS instrument on TS-II, perhaps optimised for low-Q, is being discussed, as too is the future of LOQ.

This section on SANS instrumentation is concluded with some examples of recent work conducted on LOQ. The first, taken from the authors own work, shows the changes in the SANS pattern from synthetic rope fibres under strain (Figure 6) [8]. The second example is very possibly the most technically demanding experiment ever conducted on LOQ, involving *in-situ* real-time temperature-jump measurements (Figure 7) [9].

There are two other instruments at ISIS that warrant mention in this report:

Single crystal (Laue) diffraction

SXD is a general purpose Laue diffractometer, but operating under the principles of tof [10]. It is also equipped with two-dimensional detectors, and together this allows it to simultaneously survey large volumes of reciprocal space in a

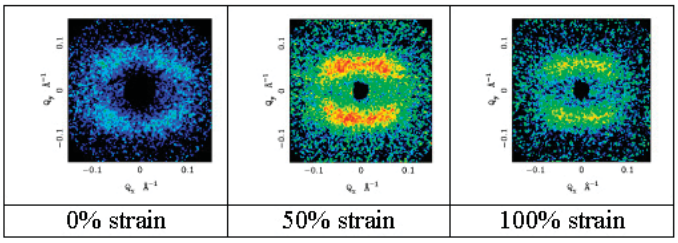

Figure 6. The scattering from nylon fibres hydrated with D2O (to the same intensity-colour scale) [8]. The sample size was approximately 30 (long) x 3 (wide) x 1 mm (thick) and was illuminated with a vertical 8 x 2 mm slit. Each pattern represents about a 40 minute exposure.

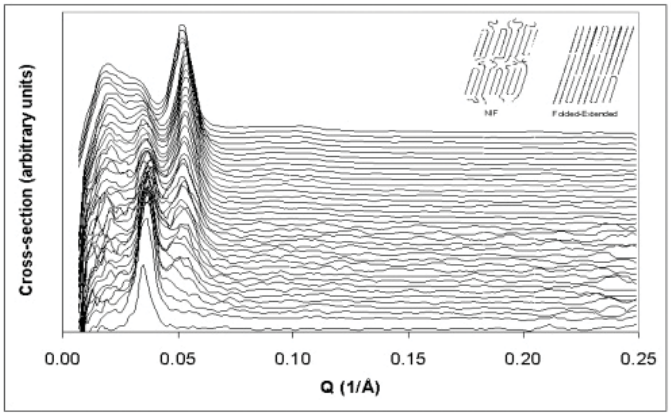

Figure 7. The SANS from the synthetic alkane $C_{12}D_{25}C_{192}H_{384}CHDC_{11}D_{23}$ isothermally crystallised at 110ºC, showing the transition from the non-integer folded to folded-extended configurations [9]. These data, displaced vertically for clarity, represent a contiguous time series of just over 20 minutes. The first 20 scattering curves are 10 *second* exposures! The sample was approximately 10 mm in diameter and 1 mm thick.

single measurement. So unlike a "conventional" Laue diffractometer it is not necessary to repeatedly rotate the sample or detectors to access all of the reflections.

The instrument underwent a major upgrade between 1999-2001 that brought the total number of detector banks up to 11 (SXD-II). The low-angle coverage has also been substantially improved (Figure 8).

The sample volumes required are typically around 100 mm^3, but ultimately depend on the unit cell size and the scattering characteristics.

A fibre diffraction program has yet to be established on SXD. Poor detector performance and poor angular coverage hampered early experiments, but both of these issues have now been addressed.

A "second-generation" instrument, LMX (the Large Molecule Crystallography diffractometer), has been proposed for TS-II and was added to the "Day Two" instrument short list by the TS-II Science Advisory Council in June 2003.

The LMX design calls for upwards of 10^5 detector pixels with higher efficiency than at present; partly to take advantage of a flux increase of perhaps as much as x40, and partly to offer substantially improved detector spatial resolution. Together

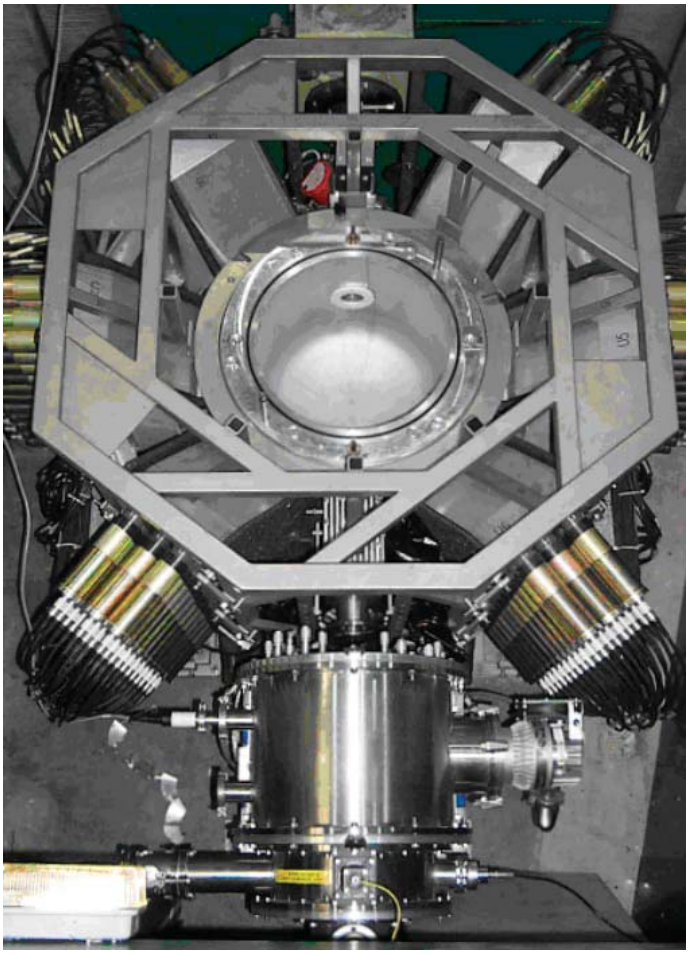

Figure 8. View of the SXD-II single crystal diffractometer sample position, showing the new jaws assembly at the bottom and some of the additional detector banks funded by the recent upgrade. In this view the incident neutron beam travels upward from the bottom centre. The sample and sample environment sit in the cylindrical well in the centre of the image. © ISIS.

these factors should make LMX highly complementary to instruments like D19 at the ILL for fibre diffraction studies, and provide a second instrument (alongside LADI at the ILL) for the study of single crystals with small unit cells.

Amorphous diffraction

GEM, the GEneral Materials diffractometer, is the newest addition to the ISIS instrument suite (Figure 9). It has been especially designed for high-intensity, high-resolution, powder diffraction from disordered and crystalline samples [11]. Already GEM has demonstrated that it is capable of measuring refinable patterns in just a few seconds (in the case of favourable samples), or patterns from samples weighing just a couple of milligrams in around 10 hours.

One of the principal features of GEM is its enormous angular coverage; 6550 scintillator detector elements (of which over 98% are already installed) spanning $1° \leq 2\theta \leq 170°$.

The capabilities of GEM have recently been used to evaluate the conformational changes that may accompany the formation of mesophases prior to crystallisation in synthetic polymers (Figure 10).

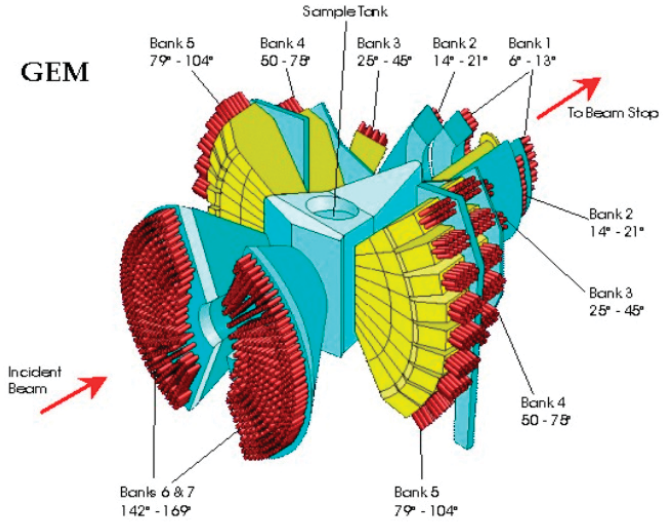

Figure 9. Schematic isometric view of the GEM powder diffractometer, including the layout of its detector banks. © ISIS.

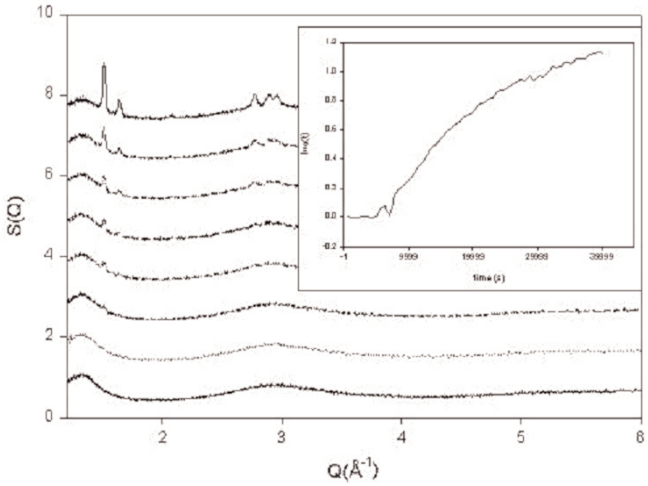

Figure 10. Wide-angle neutron scattering data from a sample of perdeuterated linear polyethylene quenched from the melt at 155ºC to 129ºC, as recorded on the GEM 25°-45° detector bank (Siripitayananon/Mitchell, 2003). The data was accumulated on a cycle time of 600 s. The curves represent data recorded at increasing time periods (since the sample was quenched) and follow the isothermal crystallisation process. The inset shows how the height of the first crystalline peak (110) at Q~1.5 Å^{-1} changes with time. These data show that GEM can record high quality broad-Q scattering data up to Q~50 Å^{-1} in the time period before the crystalline peaks can be observed.

Summary and conclusions

December 2004 will herald the 20th Anniversary of the production of the first neutrons at ISIS. In the intervening years ISIS has matured into a vibrant User Facility whose instruments now support over 1500 researchers worldwide.

The TS-II Upgrade will ultimately double the size of the instrument suite and, in areas such as solution scattering, fibre diffraction, and small-molecule crystallography, also offer significant count rate gains with improvements in resolution and Q-ranges.

The complementary nature of neutrons and X-rays is now widely recognised, the benefits are appreciated, and the gap between sample exposure times is diminishing. Real-time experiments, if not at the sub-second timescale, are becoming a reality on modern neutron instrumentation.

Shortly before TS-II becomes operational the Diamond Light Source will have delivered beam to its instrumentation. Diamond is situated at the same site (the Rutherford Appleton Laboratory) as ISIS and there is a determination to ensure that maximum benefit is extracted from the co-location of these two important facilities.

Whether you are a neutron practitioner or an X-ray practitioner, the future is bright.

Acknowledgements

I would like to thank Goran Ungar, X. Zeng (Sheffield University) and Steve Spells (Sheffield Hallam University) for allowing me to include Figure 7, and Jintana Siripitayananon and Geoffrey Mitchell (University of Reading) for allowing me to include Figure 10.

References

[1] http://www.clrc.ac.uk
[2] http://www.isis.rl.ac.uk
[3] http://sinq.web.psi.ch
[4] Heenan, R.K., Penfold, J., King, S.M. (1997) SANS at Pulsed Neutron Sources, *J. Appl. Cryst.*, **30**, 1140.
[5] Lovesey, S.W. (1986) *Theory of Neutron Scattering from Condensed Matter*, Oxford University Press.
[6] http://www.isis.rl.ac.uk/LargeScale/LOQ/loq.htm
[7] http://www.isis.rl.ac.uk/targetstation2/
[8] King, S.M., Bucknall, D.G., Heenan, R.K. (2004) SANS from Surfactant Treated Nylon Fibres, *ibid*.
[9] Zeng, X.B., Ungar, G. (2003) Triple-Layer Superlattice in Deuterium-Labeled Binary Ultralong Alkanes, *Macromol*., 36, 4686. (additional work is still in progress).
[10] http://www.isis.rl.ac.uk/crystallography/sxd/
[11] http://www.isis.rl.ac.uk/disordered/gem/gem_home.htm

Further reading

King, S.M. (1999) Small-angle neutron scattering. Chapter 7 in Modern Techniques in Polymer Characterisation. Pethrick, R.A., Dawkins, J.V. (editors).